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Iron and Chromium Removal from Binary Solutions of Fe(III)/Cr(III) and Fe(III)/Cr(VI) by Biosorbents Supported on Zeolites

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Abstract. The removal of metallic ions from binary aqueous solutions of Fe(III)/Cr(III) and Fe(III)/Cr(VI) by an *Arthrobacter viscosus* biofilm supported on NaY zeolite was investigated. Experiments were repeated with suspended biomass for comparison purposes. Batch assays were performed using different concentrations (10, 25 and 40 mg/L), for both metals in solution. Results indicated that *Arthrobacter viscosus* is able to retain the metallic ions, although not totally. The removal efficiencies were improved when the biofilm was supported on the zeolite, for all the initial concentrations of Cr(III), for the intermediate and higher concentration of Cr(VI) and for all range of initial concentrations of Fe(III), in the presence of Cr(III). The bacteria reduce Cr(VI) to Cr(III) and, only then, this cation may be entrapped in the framework zeolite by ion exchange. Suspended bacteria had higher affinity for Fe(III), than for Cr(VI) or Cr(III), while the conjugated system was selective to Fe(III) when in the presence of Cr(VI). For solutions of Fe(III)/Cr(III), very high removals were achieved by the supported system, ranging from 94 to 100 % for Cr(III) and from 98 to 100 % for Fe(III). The conjugated system also reached the highest removal ratio of Cr(VI), 36 %, for the initial concentration of 40 mg/L. The materials in study were characterized by techniques such as FTIR, SEM and chemical analyses.

Introduction

Industrial effluents contaminated with metals cause a significant threat to human health and to the environment. Iron and chromium are common pollutants which are frequently encountered together in many industrial wastewaters. Hexavalent chromium is toxic to animals and humans, is known to be carcinogenic and is reported to bio accumulate into flora and fauna, creating ecological problems [1]. Several physicochemical techniques have been used for the removal of metals, including precipitation, coagulation, reduction, membrane processes, ion exchange and adsorption [2]. However, these conventional methods are often cost prohibitive, with inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/L [3]. Thus, new technologies for treatment of metals contaminated wastewater are needed. A new system for metals removal combines biosorption by a bacterium with the ion exchange capacity of a zeolite.

The term biosorption is used to indicate a number of metabolism-independent processes (physical and chemical adsorption, ion exchange, complexation, chelation and micro-precipitation) taking place essentially in the cell wall. The main advantages of this process are cost effectiveness and good removal performance [2]. Among the different bacteria used for metals biosorption, *Arthrobacter viscosus* appears as a good exopolysaccharide producer which, by itself, allows foreseeing good qualities for support adhesion and for metal ions entrapment [4].

Various treatment processes are available for heavy metals removal, among which ion exchange is considered to be cost effective if low cost ion exchangers such as zeolites are used [5]. Zeolites are crystalline microporous aluminosilicates based on three-dimensional frameworks of SiO_4^{4-} and

AlO_4^{5-} tetrahedra which possess a net negative charge that requires the presence of organic and inorganic cations to maintain the electroneutrality of the solid [6].

Although much research has been carried out on the uptake of single species of metal ions, wastewater may contain many metallic ions and consequently competitive phenomena can occur. Multiple metals cause interactive effects depending on the number of metals competing, the combination of these metals, initial metal concentrations, the equilibrium steady state concentration of the different metal and limitations presented by the binding sites [3]. Bioremoval of single metal ions using microorganisms is affected by several factors including the specific surface properties of the organism and the physicochemical parameters of the solution such as temperature, pH, initial metal-ion concentration and biomass concentration [7].

The goal of the present work is the design of a material that may act as a robust and low cost biosorbent for treatment of wastewater with low concentration of metals ions, such as chromium and iron. This study compares the ability of an *Arthrobacter viscosus* biofilm supported on NaY zeolite and of the suspended bacterium to uptake metallic ions in binary solutions of Fe(III)/Cr(III) and Fe(III)/Cr(VI) and investigates the selectivity of the above systems towards these metals.

Experimental

Materials and reagents. *Arthrobacter viscosus* was obtained from the Spanish Type Culture Collection of the University of Valência. The binary solutions were prepared by diluting $FeCl_3.6H_2O$ (Riedel) and $CrCl_3.6H_2O$ (Merck) or $K_2Cr_2O_7$ (Panreac) in distilled water. The NaY zeolite (Si/Al = 2,83) with specific surface area of 900 $m^2.g^{-1}$, were obtained from Zeolyst International. The zeolite was calcined at 500 ºC during 8 hours under a dry air stream prior to use.

Methods. A medium with 10 g/L of glucose, 5 g/L of peptone, 3 g/L of malt extract and 3 g/L of yeast extract was used for the microorganism growth. The medium was sterilized at 121 ºC for 20 min, cooled to room temperature, inoculated with bacteria and kept at 28 ºC for 24 h with moderate stirring in a incubator. Then, batch experiments were conducted using 1 g of the NaY zeolite with 15 mL of *A. viscosus* culture media and 150 mL of the different binary solutions with concentrations of each metal of 10, 25 and 40 mg/L, in 250 mL Erlenmeyer flasks. Experiments were repeated just with suspended biomass, i.e. without the zeolite for comparison purposes. All experimental work was conducted in duplicate. The Erlenmeyer flasks were kept at 28 ºC, with moderate stirring until equilibrium was reached. Samples of 1 mL were taken, centrifuged and analyzed for metals using Atomic Absorption Spectrometry (AAS). After the experimental studies, the obtained zeolite samples were centrifuged and dried at 60 ºC for 3 days. The samples have been identified by designation Fe(III)/Cr(III)$_n$-Y and Fe(III)/Cr(VI)$_n$-Y, where n represents the initial concentration (mg/L) of both metals in the solution.

Total metal ions concentrations were measured by AAS, using a Varian Spectra AA-400. Room temperature FTIR spectra of zeolites were obtained from powdered samples on KBr pellets, using a Bomem MB104 spectrometer in the range (4000-500) cm^{-1} by averaging 20 scans at a maximum resolution of 10 cm^{-1}. The morphology of NaY zeolite was evaluated by scanning electron microscopy (SEM), using a Leica Cambridge S360. The elemental chemical analyses (Cr and Fe) were performed by University of Minho, Departamento de Ciências da Terra, using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Results and Discussion

Fig. 1 shows the dependence of the chromium and iron removal efficiencies, as function of the initial concentration of each metal in solution, and compares the performance of both systems in study, the supported system – bacteria/zeolite – and the suspended bacteria, on metals uptake.

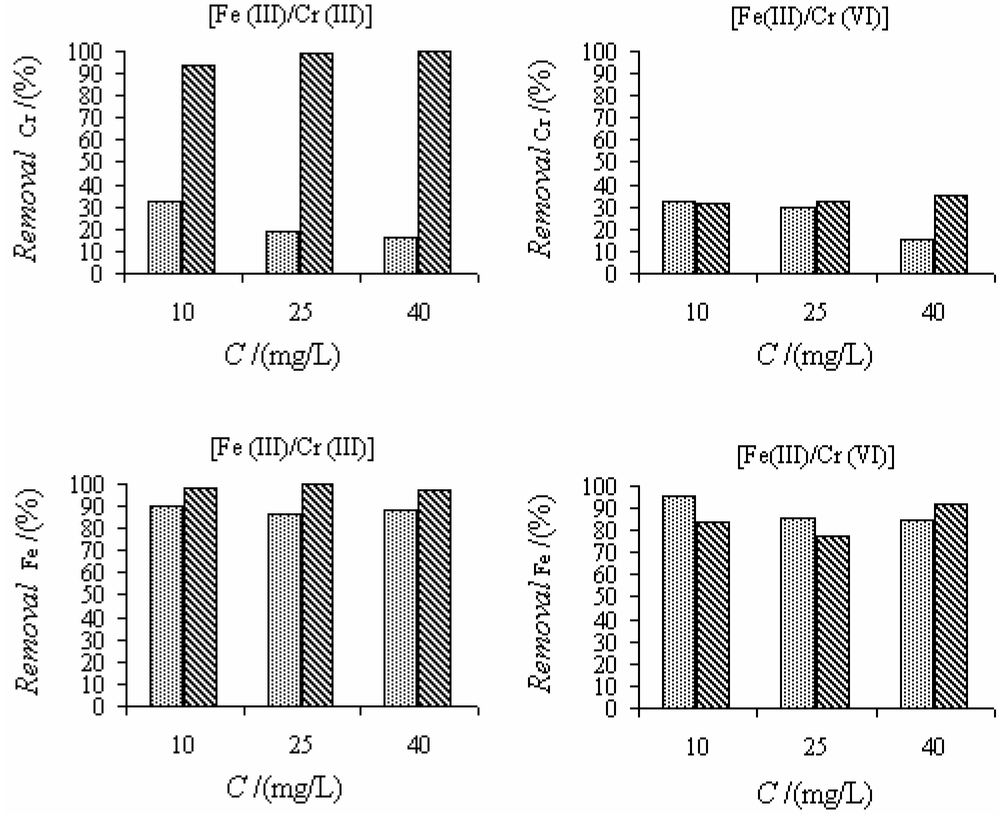

Fig. 1. Removal efficiency of Cr(III), Cr(VI) and Fe(III) for initial binary solutions of Fe(III)/Cr(III) and Fe(III)/Cr(VI): suspended *A. viscosus* ( ) and *A. viscosus* supported on NaY zeolite ( ).

It can be seen that Cr(III) is easily removed from solution in the presence of the supported system, with removal efficiencies ranging from 94 to 100 %. This is due to the positive charge of the metal that enhances the entrapment in the framework zeolite by ion exchange. In terms of Cr(VI) ions removal, comparison between bacteria in suspension and supported on NaY zeolite shows better performance of supported system for the intermediate and higher concentration of Cr(VI), which is more obvious as the initial metal concentration increases. The conjugated system performed the highest removal ratio of Cr(VI), 36 %, for initial concentration of 40 mg/L. The bacteria perform an important role on the reduction of Cr(VI) to Cr(III) allowing the entrapment of the cation in the framework zeolite by ion exchange. The removal efficiencies of Fe(III) were improved when the biofilm was added to the zeolite for the whole range of initial concentrations of Fe(III), in the presence of Cr(III), and for the higher initial concentration in the presence of Cr(VI). The highest iron removal efficiency, 99.7 %, was achieved by the supported system in the presence of Cr(III), for initial concentration of 25 mg/L.

To evaluate possible metal precipitation, solution pH values were recorded during the experiments. The range of pH (initial and final) is presented in Table 1.

Table 1 - Variation of solution pH values during the experiments

	Fe(III)/Cr(III)			Fe(III)/Cr(VI)		
	10 mg/L	25 mg/L	40 mg/L	10 mg/L	25 mg/L	40 mg/L
Bacteria	4.17 – 7.71	3.91 – 5.13	3.50 – 5.11	4.26 – 8.21	4.35 – 5.27	3.81 – 4.43
Bacteria and zeolite	5.86 – 8.05	6.06 – 7.42	5.66 – 7.03	5.61 – 8.19	6.21 – 8.37	5.89 – 7.49

Precipitates such as $FeOHCrO_4$, $FeOHCrO_4 \cdot 2Fe(OH)_3$ and $Fe(OH)_3$ may occur in binary solutions of Fe(III)/Cr(VI) [8], while $Cr(OH)_3$ and $Fe(OH)_3$ may appear in Fe(III)/Cr(III) solutions. Considering the solubility product constants of these precipitates, K_{ps}, the pH values and the metal concentration profiles in solution, the formation of chromium precipitates can be excluded. On the other hand, precipitation of $Fe(OH)_3$ probably occurs during the experiments with the zeolite, due to its capacity of increasing the pH of the solution. However, due to the high iron removal efficiencies performed by the zeolite, the precipitate formed can be considered as residual.

The selectivity of suspended bacteria and the supported system for transition metals, as well as the influence of each competitive ion in the removal mechanism, were evaluated. The selectivity ratios for the two pairs of metals in solution are presented in Fig. 2. For a given couple of metals in solution, M_1/M_2, the selectivity ratio (S) can be calculated by Eq. 1.

$$S = \frac{R_{\mathrm{M_1}}(t)}{R_{\mathrm{M_2}}(t)} \tag{1}$$

where $R_{\mathrm{M_i}}(t)$ represents the removal efficiency of the metal M_i at the time t.

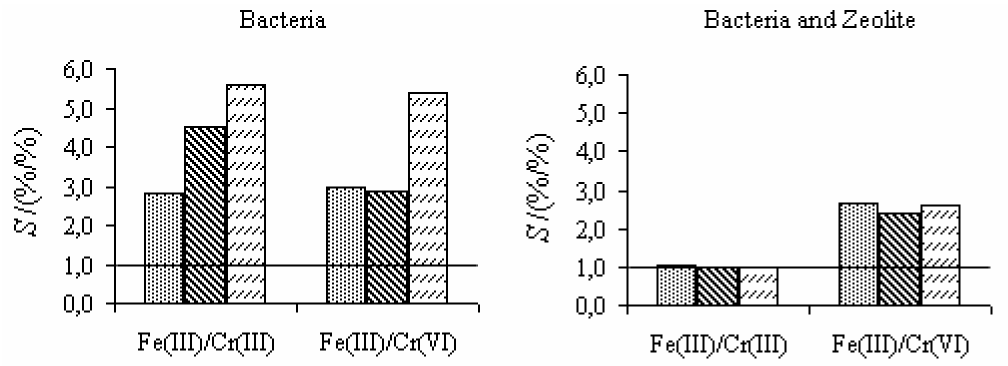

Fig. 2. Two-component selectivity ratios for bacteria in suspension and supported system, as a function of the initial concentration of metals in solution: 10 mg/L ( ), 25 mg/L ( ) and 40 mg/L ( ).

It can be seen that bacteria in suspension had higher affinity for Fe(III), compared to Cr(VI) or to Cr(III). The selectivity of suspended bacteria towards Fe(III) increased with metal concentration, in the presence of Cr(III), and only significantly for the higher concentration when Cr(VI) was in solution. The supported system was not selective for Fe(III) nor Cr(III), since selectivity ratios are near to 1, being selective for Fe(III) just in the presence of Cr(VI). For the supported system and metal couples of Fe(III)/Cr(III) and Fe(III)/Cr(VI) the selectivity seems to be concentration-independent.

The morphology of the NaY zeolite after the uptake process was evaluated by SEM, as presented in Fig. 3. It can be seen the bacterium biofilm on the zeolite surface with a considerable production of exopolysaccharide that provides a good adhesion to the support. Comparison between SEM photographs of the starting NaY (not showed) and those of the modified zeolites indicates that the particle size and morphology remained unchanged after the removal of the metal ions.

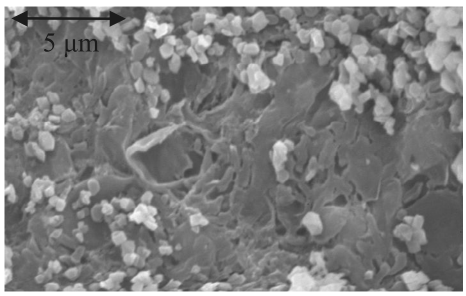

Fig. 3. SEM photograph of Fe(III)/Cr(III)$_{40}$-Y.

The weight percentage of metal loadings in NaY zeolite after biosorption, obtained by bulk chemical analyses, is presented in Table 2. The amount of Cr and Fe taken up by the zeolite after the biosorption process increased with the concentration of the metals in solution, for the range between 10 and 40 mg/L. Chemical analyses are in agreement with the results presented above, relative to the removal efficiencies and selectivity ratios.

Table 2 - Chemical analyses of the zeolite samples after biosorption process, (wt%)

	Fe(III)/Cr(III)$_{10}$-Y	Fe(III)/Cr(III)$_{25}$-Y	Fe(III)/Cr(III)$_{40}$-Y	Fe(III)/Cr(VI)$_{10}$-Y	Fe(III)/Cr(VI)$_{25}$-Y	Fe(III)/Cr(VI)$_{40}$-Y
Fe (wt %)	0.15	0.32	0.48	0.11	0.15	0.40
Cr (wt %)	0.11	0.28	0.45	0.06	0.06	0.20

Structural information of the zeolite samples has been obtained by FTIR spectroscopy. The FTIR spectra in the range (4000–500) cm^{-1} are presented in Fig. 4 for the starting NaY, Fe(III)/Cr(III)$_{40}$-Y, Fe(III)/Cr(VI)$_{40}$-Y and *A. viscosus* bacterium. No shift or broadening of zeolites vibrations are observed upon inclusion of chromium and iron by the biosorption process, which indicates that the framework zeolite remains unchanged. In the modified zeolite spectrums (Fig.4 – B, D), the presence of the bacteria can be only detected by a band at 1400 cm^{-1} and a weak band at 2925 cm^{-1},where the zeolite does not absorb [9].

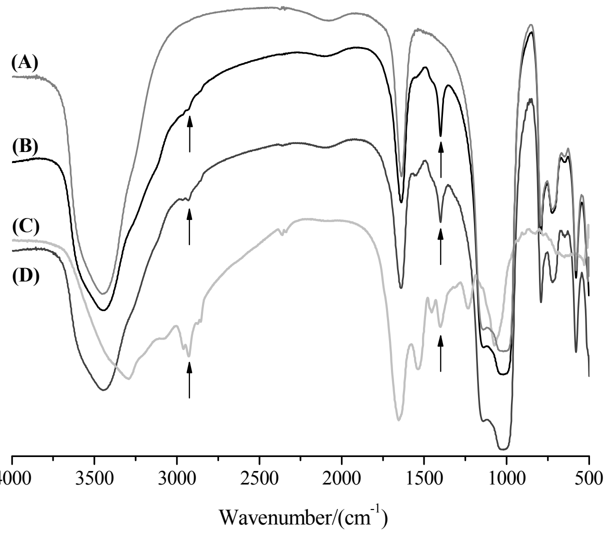

Fig. 4. FTIR spectra in the range (4000-500) cm^{-1} for: NaY **(A)**, Fe(III)/Cr(III)$_{40}$-Y **(B)**, *A. viscosus* bacterium **(C)** and Fe(III)/Cr(VI)$_{40}$-Y **(D)**.

Conclusion

A new system can be applied to the treatment of wastewater with low concentration of metals ions. A biofilm of *Arthrobacter viscosus* supported on NaY zeolite shows better performance on the removal of metals in binary solutions of Fe(III)/Cr(III) and Fe(III)/Cr(VI) than the suspended bacteria. The biofilm has an important role on the reduction of Cr(VI) to Cr(III) that allows the ion exchange of this cation in the zeolite. FTIR and SEM results show that this biosorption process does not have an effect on the morphology and structure of the NaY zeolite.

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